APPENDIX B. CARBON SEQUESTRATION PROJECTS, INITIATIVES AND TECHNOLOGIES

This appendix provides details about existing and ongoing carbon sequestration research projects, initiatives and technologies. Although some of the projects and initiatives described here are being sponsored by DOE, the majority are sponsored by other government agencies, the private sector, or foreign governments. These descriptions are provided for both:

- technologies that are in the very earliest stages of research, where deployment at the demonstration or commercial scale would not occur before 2012, and
- existing and ongoing projects in the U.S and other countries, where the descriptions help exemplify the types and scales of research being conducted around the world.

Technologies and related projects described in this appendix include:

- Pre-Combustion Decarbonization
- Post-Combustion Capture
- Oxygen-Fired Combustion
- Advanced Conversion
- Sequestration in Coalbeds
- Enhanced Oil Recovery and Enhanced Gas Recovery
- Sequestration in Saline Formations
- Sequestration in Other Novel Formations
- Terrestrial Sequestration
- Ocean Fertilization
- Deep Ocean Injection of CO_2
- Geologic Sequestration MM&V
- Terrestrial Sequestration MM&V
- Breakthrough Concepts
- Non-CO_2 Greenhouse Gas Mitigation

B.1 PRE-COMBUSTION DECARBONIZATION

Pre-combustion decarbonization involves the removal of carbon from a gaseous, liquid, or solid fuel before it is burned through various approaches. A very promising technology involves gasifying coal and then scrubbing the CO_2 from the fuel gas before combustion. The CO_2 is normally removed by a chemical or physical absorption system. Existing capture technologies operate at a low temperature, requiring the synthesis gas (syngas) produced in the gasifier to be cooled for CO_2 capture and then reheated before combustion in a turbine (Klara and Srivastava, 2002). There are 10 oxygen-fired gasifiers in operation in the U.S. today. Syngas from an oxygen-fired gasifier can be shifted to provide a stream primarily of hydrogen (H_2) and CO_2 at 400-800 pounds per square inch (psi). Glycol solvents can capture CO_2 and be regenerated via flash (no steam use) to produce pure CO_2 at 15-25 psi (NETL, 2005b). Substantial cost reductions in CO_2 capture and separation are expected to come through integrated designs incorporating the use of membranes and other breakthrough recovery technologies.

B.1.1 CO_2 Separation Using a Selective Ceramic Membrane

The water-gas shift (WGS) reaction can increase the H_2 content of a syngas, but the reaction is equilibrium-limited. The fact that the reaction is equilibrium-limited means that the reaction is capable of going in either the forward or reverse direction. That is, it is also possible for CO_2 and H_2 to combine to form carbon monoxide (CO) and water, as steam, under conditions that are favorable for this backward reaction.

One approach for overcoming this limitation is to use a reactor in which the walls are CO_2-permeable, allowing the CO_2 to be removed from the system and the reaction to continue:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The WGS reactor has catalyst-filled ceramic tubes with a membrane that is selectively permeable to CO_2. As gasifier fuel gas passes through the WGS reactor, CO_2 diffuses through the membrane allowing the reaction to approach completion. This process generates a hydrogen-rich fuel stream, while simultaneously producing a pure CO_2 stream for sequestration.

A current project sponsored by NETL is developing a technique for depositing hydrotalcite onto a ceramic membrane suitable for studying the CO_2 separation concept with the WGS reaction in an IGCC system (NETL, 2003). The hydrothermal and chemical stability in a simulated WGS reaction environment will be evaluated to confirm the inert material properties of the ceramic membrane. Then, a membrane reactor (MR) study will be performed to demonstrate the benefit offered by this membrane. Finally, process feasibility will be demonstrated in a test module, and an economic evaluation will be performed to estimate the positive effect of using a WGS-MR in IGCC coal-fired power plants.

This project will produce a hydrogen-rich gas that is at high pressure and high temperature and that contains significant quantities of steam, making it highly suitable for direct firing in a gas turbine with high efficiency. The use of an improved WGS-MR with CO_2 recovery capability is ideally suited for integration into the IGCC power generation system. Thus, the hydrogen (at high pressure and CO_2-free) produced from the IGCC can be used as a product for power generation via a turbine or a fuel cell, or it can be used as a reactant for production of fuels and chemicals.

In another project, which was awarded by NETL in 2004, researchers at the University of Minnesota will develop a new method for making extremely thin, high-temperature, hydrogen-selective silica membranes from byproduct materials (NETL, 2004l). The membranes, called molecular sieves, work like filters with uniquely designed, ultra-small pores that allow only hydrogen molecules to pass through, leaving behind a CO_2-rich gas for sequestration. Such membranes will potentially be used in future fossil-fueled power plants that produce hydrogen under conditions of high temperatures and pressures.

B.1.2 CO_2 Separation through the Formation of Hydrates

Another approach for decarbonizing a syngas utilizes the formation of CO_2 hydrates to remove CO_2 from a gas stream. Under suitable conditions, CO_2 can form hydrates, which are ice-like complexes of water and CO_2 molecules. The CO_2 hydrates are similar to methane hydrates, in which a methane molecule is enclosed in a cage of water molecules. Because viable options for sequestration or reuse of CO_2 are expected to involve transport through pipelines and/or direct injection of high-pressure CO_2 into various repositories, a process that can separate CO_2 at high pressures and minimize recompression costs will offer distinct advantages.

An R&D project sponsored by NETL addresses the issue of CO_2 separation from shifted syngas at elevated pressures using a low-temperature process (NETL, 2004d). The goal of this project is to construct and operate a pilot-scale unit utilizing the hydrate process for CO_2 separation. The objectives of current work in this area are to: (1) carry out further laboratory-scale tests of the CO_2 hydrate concept, including extended continuous-flow tests and component tests; (2) conduct an engineering analysis of the concept, and develop updated estimates of the process performance and cost of carbon control; and (3) use data developed in the lab to design and build a pilot plant using a slipstream in an operating IGCC plant. Future efforts will consist of a pilot demonstration of the process in the IGCC plant.

The hydrate process will provide a high-pressure/low-temperature system for separating CO_2 from shifted syngas in an economical manner. The process can be adapted to an existing gasification power plant for CO_2 separation during production of syngas. Ultimately, the process will result in a residual concentrated stream of hydrogen capable of fueling zero-emission power plants of the future and a concentrated CO_2 stream available for use or sequestration.

B.1.3 CO_2 Separation Using Polymer Membranes

Polymer membranes are employed in many industrial gas separation applications, including the production of high-purity nitrogen, natural gas, dehydration and removal of acid gases, and hydrogen recovery from process streams. Many gas separation applications require materials that are stable at high temperatures and pressures. Polymeric materials currently in commercial use have thermal and mechanical limits too low for such applications. Hence, there is a need for membrane materials that can operate under more extreme conditions for extended periods of time while providing an acceptable level of performance (Klara and Srivastava, 2002 and DOE, 1999). Organic polymer membranes have superior selectivity, while inorganic membranes have superior permeability and stability. Thus, the development of hybrid organic and inorganic membranes may potentially yield the advantages of both types of membranes (NETL, 2004i).

In a project sponsored by NETL, collaborators, including Los Alamos National Laboratory and Idaho National Energy and Engineering Laboratory, are developing a high-temperature polymeric membrane that will exhibit selectivity for CO_2 at an order of magnitude higher than current membranes (NETL, 2004e). The project will focus on the separation of CO_2/CH_4, CO_2/N_2, and H_2/CO_2 gas pairs, which represent separations that are industrially and environmentally important. The major objective of the project is the development of polymeric materials that achieve the important combination of high selectivity, high permeability, and mechanical stability at high temperatures and pressures.

The development of high temperature polymeric-metallic composite membranes for CO_2 separation at temperatures of 100-450°C and pressures of 10-150 bar will provide a pivotal achievement with both economic and environmental benefits. This technology could further reduce the cost of CO_2 sequestration by providing a CO_2 stream at higher pressures than existing technologies, thereby reducing compression costs significantly.

B.2 POST-COMBUSTION CAPTURE

The following are examples of R&D efforts and pilot projects for post-combustion capture sponsored by NETL.

B.2.1 Absorption with Potassium Carbonate

Expanding on bench-scale modeling and pilot-scale experiments, the University of Texas is researching an alternative alkanolamine sorbent (NETL, 2004f). In early experiments, the promotion of potassium carbonate (K_2CO_3) with amines, such as K_2CO_3 in solution with catalytic amounts of piperazine (PZ), exhibited an absorption rate comparable to MEA. Studies also indicate that PZ has a significant reaction rate advantage over other amines as additives. The latest improved process uses a highly reactive solvent that absorbs CO_2 three times faster than MEA and requires as much as 40 percent less energy per unit of CO_2 captured. The process model will be validated by a pilot-plant study to optimize solvent rate, stripper pressure, and other parameters.

B.2.2 Ionic Liquids as Novel Carbon Dioxide Absorbents

In a project awarded by NETL in early 2004, the University of Notre Dame will focus on the development of liquid absorbents that fall within a relatively new class of compounds called ionic liquids (NETL, 2004l). Ionic liquids are typically organic salts that, in their pure state, are liquid under atmospheric conditions at room temperature. They have unusual properties that suggest they could be extremely effective as CO_2 absorbents, possibly replacing current amine-based technology to capture CO_2 from power plant stacks. Unlike amines, which are corrosive and costly to operate, organic salts are typically benign, and can be disposed of in landfills. Building upon and extending their previous work with other chemicals, the researchers will use computer modeling to design and evaluate ionic liquids to determine their affinity for capturing CO_2. They will also assess the economics of different ionic liquids against conventional absorbents.

B.2.3 Dry Regenerable CO_2 Sorbents

Another approach to CO_2 capture employs dry scrubbing by chemical adsorption with a dry sorbent. Such a sorbent can remove CO_2, be regenerated to produce a concentrated stream of CO_2, and be returned to capture more CO_2 in a cyclical process. This process can have economic advantages compared to commercially available wet-scrubbing amine processes. NETL has pioneered R&D to identify dry, regenerable sorbents that can be used for CO_2 capture. Preliminary micro-reactor tests with sodium carbonate have indicated that absorbing CO_2 and steam to form bicarbonate, with subsequent regeneration to the carbonate, is a viable process. Because sorbent regeneration uses waste heat, the power requirement for CO_2 capture is relatively small (Klara and Srivastava, 2002).

In one R&D project, the Research Triangle Institute and Church and Dwight, Inc. are developing an innovative process for CO_2 capture that employs a dry, regenerable sorbent (NETL, 2003a). The goal of this project is to develop a simple, inexpensive process to separate CO_2 as an essentially pure stream from a fossil fuel combustion system. The proposed process can also be used to capture CO_2 from gasification streams at high temperature. Sorbents being investigated, primarily alkali carbonates, are converted to bicarbonates through reaction of CO_2 and water vapor. Sorbent regeneration produces a gas stream containing only CO_2 and water. The water may be separated out by condensation to produce a pure CO_2 stream for subsequent use or sequestration. Future efforts will be aimed at optimizing the process to capture additional CO_2 without requiring additional power.

B.2.4 Pressure and/or Temperature Swing Adsorption

Selective separation of CO_2 can be achieved by the preferential adsorption of the gas on high-surface area solids. Conventional physical adsorption systems are operated in pressure swing adsorption (PSA) and temperature swing adsorption (TSA) modes. In PSA, the gas is absorbed at a higher pressure; then pressure is reduced to desorb the gas. In TSA, the gas is absorbed at a lower temperature; then the temperature is raised to desorb the gas. PSA and TSA are some of the potential techniques that could be applicable for removal of CO_2 from high-pressure gas streams, such as those encountered in IGCC (NETL, 2002).

B.2.5 Electric Swing Adsorption

Electric Swing Adsorption (ESA) is an advanced separation system for CO_2 removal from syngas being developed for use with the gasification of low hydrogen-to-carbon ratio fuels, such as petroleum coke. Oak Ridge National Laboratory has developed a novel process, which adsorbs CO_2 on a carbon substrate. After saturation of the carbon fiber adsorbent with CO_2, immediate desorption of the adsorbed gas is accomplished by applying low voltage across the adsorbent. This technology is being developed to remove CO_2 from the exhaust gas of a conventional combined cycle turbine. Calculations based on adsorption data indicate that it should be possible to develop an improved CO_2 separation process using this method (Klara and Srivastava, 2002).

B.2.6 Gas-Separation Membranes

Gas-separation membranes are of many different types, and although the effectiveness of only a few of these types in separating and capturing CO_2 has been demonstrated, their potential is generally viewed as effective. Gas separation is accomplished via interaction between the membrane and the gas being separated. For example, polymeric membranes transport gases by a solution-diffusion mechanism (i.e., the gas is dissolved in the membrane and transported through it by a diffusion process). Polymeric membranes, although effective and inexpensive, typically achieve low gas transport flux and are subject to degradation. Considerable R&D is required to realize the potential of membranes for separation and capture of CO_2, particularly at higher temperatures and pressures. R&D on polymeric membranes is essentially restricted to changing the composition of the polymer to increase the dissolution and diffusion rates for the desired gas components out of the gas stream and through the membrane. Experience shows an apparent limit to the efficacy of polymeric membranes. Inorganic membranes may be developed to reform fuels to mixtures of hydrogen and CO_2, and to separate the hydrogen with the remaining CO_2 recovered in a compressed form. Major issues include capital cost and membrane stabilization in corrosive gases for coal use (DOE, 1999).

NETL awarded a project in early 2004 that will develop a novel membrane for controlling CO_2 emissions from fossil fuel power plants (NETL, 2004l). Researchers at the University of New Mexico in collaboration with T3 Scientific will develop a new, dual-functional membrane that will use both the pore structure of the membrane, and an amine chemical adhered to the membrane, to increase the removal of CO_2 from fossil-fueled power plants. Researchers anticipate that the strong interactions between the CO_2 molecules and the amine-coated membrane pores will help spread the CO_2 on the pore walls and block other gases, such as O_2, N_2, and S_2O, that are also present in power plant stacks. The new membrane is expected to exhibit higher CO_2 selectivity than other types of silica-based membranes that separate CO_2 based only on the difference in pore size. This new membrane-based CO_2 capture process may be an attractive alternative to costly amine-based absorption processes.

B.2.7 Novel Microporous Metal Organic Frameworks

NETL awarded a project in early 2004 that will involve a collaborative effort among United Oil Products LLC, the University of Michigan, and Northwestern University to discover novel microporous metal organic frameworks (MOFs) suitable for CO_2 separation (NETL, 2004l). MOFs are hybrid organic/inorganic structures at the nanoscale (submicroscopic) to which CO_2 will stick. Researchers plan to use molecular modeling on computers to design, tailor, and assess MOFs with the best properties for adsorbing CO_2, and to predict structures of new MOFs. Successful completion of this project will lead to a low-cost, novel sorbent to remove CO_2 from the gases emitted from power plant stacks.

B.2.8 Co-Sequestration of CO_2 with SO_2 and NO_X

DOE-NETL's Carbon Sequestration Program has a goal to develop by 2015, to the point of commercial deployment, systems for the direct capture and sequestration of greenhouse gas and criteria pollutant emissions from fossil fuel conversion processes that results in near-zero emissions. The goal also states that these systems should approach no net cost increase for energy services when any value-added benefits are factored in.

As part of the plan to achieve that goal for existing pulverized coal-fired boilers, DOE-NETL has initiated preliminary R&D scoping engineering studies to evaluate the feasibility of several processes that would sequester CO_2 and other criteria pollutants. One approach under evaluation is the use of oxygen fired combustion with flue gas recycling. This process maintains a normal temperature in the furnace, resulting in a CO_2-rich stream exiting the boiler that is ready for sequestration with only minimal gas conditioning. That project addresses both possibly retrofitting boilers at existing coal-fired power plants, such that CO_2 capture eliminates the need for N_2/CO_2 separation and sulfur separation, and permits more economical CO_2 recovery than competing amine systems. In another economic and engineering scoping study, CO_2 capture from pulverized coal boilers using aqueous ammonia is being evaluated. Aqueous ammonia has been used in several commercial power plant SO_2 capture applications, and a commercial-scale demonstration of multi-pollutant control for scrubbing SO_2, NO_X, and mercury from flue gas. As such, incorporating CO_2 capture within the aqueous ammonia scrubber system (via CO_2 capture and solvent regeneration by chemical reaction cycling between ammonium carbonate and bicarbonate) presents a potentially advantageous multi-pollutant control option for CO_2. As both of these projects are in the early stages of R&D, no model project was developed in this PEIS for the co-sequestration of CO_2 with criteria pollutants.

B.3 CO_2 CAPTURE PROJECT

In collaboration with eight major international energy companies, DOE is sponsoring the CCP with the goal of developing breakthrough technologies aimed at substantially reducing the costs of CO_2 capture and geologic storage (NETL, 2003b). The CCP consortium is led by BP-Amoco, and its members include ChevronTexaco, ENI, Norsk Hydro, PanCanadian, Shell, Statoil, and Suncor. In addition to the U.S. program, the CCP is performing separate, but complementary projects, which are being sponsored by the European Union and Norway. The CCP team collectively accounts for approximately 32 percent of all oil and 17 percent of all gas production in the U.S., and 28 percent of oil and 17 percent and gas production by Organization for Economic Cooperation and Development (OECD) countries.

The project involves an integrated CO_2 capture and sequestration undertaking. For the CO_2 capture effort, the project objectives are to perform benchtop R&D (engineering studies, computer modeling, and laboratory experiments) to prove the feasibility of advanced CO_2 separation and capture technologies. This will specifically target post-combustion capture, pre-combustion decarbonization, and oxyfuel combustion. By conservative estimates, the technology developed in the project could reduce the emissions of the CCP participants by 10 MMT of carbon per year. When applied more broadly in the energy industry, the technology could reduce emissions by up to 140 MMT of carbon per year.

Additional R&D Efforts

In addition to the projects summarized in the preceding paragraphs, NETL is sponsoring additional R&D efforts by universities and industries, and by using its own scientists and facilities (NETL, 2004b, 2002a, 2002b, 2002c, 2002d). Examples include:

- Carnegie Mellon University is developing an integrated modeling framework to evaluate alternative carbon sequestration technologies for electric power plants.
- Princeton University is developing a conceptual design of optimized fossil energy systems with capture and sequestration of CO_2.
- Siemens Westinghouse Power Corporation is modifying the design of the tubular solid oxide fuel cell (SOFC) module to incorporate an afterburner stack of tubular oxygen transport membranes, which will oxidize the SOFC-depleted fuel in the anode exhaust to CO_2 that can then be easily separated.
- NETL designed and constructed the Modular Carbon Dioxide Capture Facility (MCCF), which mimics coal-fired combustion processes that produce electricity and can be fired with natural gas, coal, or a combination of the two. The MCCF can be used to test new capture technologies on coal combustion flue gas and, additionally, on process gas from advanced fossil-fuel conversion systems, such as coal gasification (NETL, 2003c).
- The Carbon Sequestration Science Focus Area (CSSFA) at NETL serves as the focal point for all carbon sequestration R&D activities performed with in-house resources sponsored primarily by the Office of Fossil Energy. CSSFA conducts research ranging from fundamental studies to small-scale proof-of-concept research on selected processing options. Systems analysis via computer modeling and simulation of approaches to carbon sequestration will be developed in-house for use in evaluating the various approaches (NETL, 2002a).

B.4 OXYGEN-FIRED COMBUSTION

Oxygen-fired combustion burns fuel in enriched air or pure oxygen to produce a concentrated stream of CO_2. It presents significant challenges but provides high potential for technology break-throughs and step-change reduction in CO_2 separation and capture costs. Currently, there are no oxygen-fired PC plants in commercial operation. Among the barriers and issues are the facts that oxygen generation is expensive, oxygen combustion consumes three times more oxygen per kilowatt-hour (kWh) of electricity generation than coal gasification followed by combustion of the syngas in air, and combustion of fuels in pure oxygen occurs at temperatures too high for existing boiler or turbine materials. The economics of oxygen firing and IGCC can be improved by advanced oxygen production technology. New air separation processes using high-temperature oxygen ion transport ceramic membranes are being developed. For oxygen-fired combustion, the integration of an oxygen transport membrane (OTM) for oxygen production with the combustion system can provide cost-effective capture of CO_2 from power plants (NETL, 2004a and 2004b; Klara and Srivastava, 2002).

B.4.1 Advanced Oxyfuel Boilers and Process Heaters for Cost-effective CO_2 Capture

NETL, Praxair, and Alstom Power are collaborating on a project that will advance the integration of OTMs into oxy-fired boilers from the bench scale to the point-of-readiness for engineering scale-up (NETL, 2004g). The development of a novel oxy-fuel boiler will significantly reduce the complexity of CO_2 capture, drastically reduce the cost of carbon sequestration, and offer increased thermal efficiency and reduced pollution emissions. Gasification plants that integrate OTM technology will have higher efficiency, lower cost of electricity, and lower emissions of pollutants compared to a conventional cryogenic air separation unit. The main objectives of the project are: (1) to develop and demonstrate the integration of a novel ceramic OTM with the combustion process to enhance boiler efficiency and CO_2 recovery, and (2) to develop a conceptual design for a laboratory scale boiler simulator. The project has developed a ceramic membrane and seal assembly for thermal integration between the high temperature membrane and the combustion process. Current efforts focus on laboratory-scale evaluations for the integration of OTM with the combustion process.

B.4.2 Oxygen Firing in Circulating Fluidized Bed (CFB) Boilers

The goal of a project involving NETL, Alstom Power, ABB Lummus Global, and others is to conduct economic evaluations of CO_2 recovery using a newly constructed circulating fluidized bed (CFB) combustor burning various solid fuels with a mixture of oxygen and recycled flue gas, instead of air (NETL, 2004h). In Phase 1 of the project, a performance analysis of the base case (air-fired) CFB was completed to determine which of the new concepts in a CFB are technically feasible and have the potential for reducing the target cost of carbon emissions avoided. In Phase 2, the project will generate a refined technical and economic evaluation of the most promising concept, based on data from proof-of-concept testing. Work has been completed on the performance analysis of three advanced O_2-fired CFB concepts, a high-temperature carbonate regeneration process, a chemical looping concept, and two IGCC cases (a base case without CO_2 capture and one with a WGS reactor to capture CO_2). Phase 2 pilot testing has been initiated, and the test facility is being modified to perform the planned pilot tests.

B.4.3 Oxygen-enriched Combustion

CanMet Energy Technology Center and a consortium of industrial companies, including McDermott Technology, Trans Alta Corp., Saskatchewan Power, Air Liquide Canada, Nova Scotia Power, Ontario Power Generation, and Edmonton Power are conducting pilot-scale tests of oxygen enhanced coal combustion with the objective of lowering the cost of retrofit systems (NETL, 2005b).

B.5 ADVANCED CONVERSION

There is a limited number of other promising concepts for CO_2 capture, none of which is yet at a commercial or demonstration phase. One example involves the indirect combustion of coal, sometimes referred to as chemical looping, to provide oxygen for combustion by a metal oxide, rather than by air. TDA Research and Louisiana State University are collaborating on such a project for NETL. These researchers intend to develop a method using gasified coal or natural gas to reduce a metal-oxide sorbent, producing steam and high pressure CO_2. The steam will be condensed into water, and the CO_2 will be sequestered. The reduced metal-containing solid will be transferred to a second fluidized bed reactor, where it will be re-oxidized with air. This exothermic reaction heats the oxygen-depleted air, which is used for power production. Sorbent materials with desirable properties will be developed and tested, and the economics and emissions performance of integrated electricity generation systems based on the various sorbents will be estimated (Klara and Srivastava, 2002).

B.6 SEQUESTRATION IN COALBEDS

B.6.1 Effects of Temperature and Gas Mixing in Underground Coalbeds

NETL is sponsoring a bench-scale research project by Oak Ridge National Laboratory that intends to measure the behavior of CO_2, methane, and nitrogen gas mixtures at elevated temperatures and pressures (Blencoe, et al., 2004). The project will focus on temperatures (25-200º C) and pressures (1-300 bars) that are relevant to CO_2-enhanced CBM recovery. Measurements will be taken for the density and viscosity of the gas mixtures and coal swelling and shrinkage in brine-mixed combinations of the three gases. The project also intends to acquire additional technical data needed on the geochemical reactions that will occur when CO_2 is injected into deep, unmineable coalbeds.

B.6.2 Enhancing Methane Production in Unmineable Coalbeds while Sequestering CO_2

Oklahoma State University is leading a bench-scale effort to investigate and test the ability of injected CO_2 to enhance CBM production (NETL, 2002e). The effort will collect data from coals of various physical properties at various temperatures, pressures, and gas compositions to identify the conditions for which proposed sequestration applications are most attractive. The overall goal of the project is to develop predictive models for describing the adsorption behavior of gas mixtures on coal over a complete range of temperature, pressure, and coal types.

The project team is developing mathematical models to describe the observed adsorption behavior accurately. The combined experimental and modeling results will be characterized to provide a sound basis for performing reservoir simulation studies. These studies will evaluate the potential for injecting CO_2 or flue gas into coalbeds to simultaneously sequester CO_2 and enhance CBM production. Future computer simulations will assess the technical and economic feasibility of the proposed process for specific candidate injection sites.

Thus far, the project has characterized several types of coals by their ability to adsorb nitrogen, methane, and CO_2. Adsorption of CO_2 and methane at low pressure was studied in a laboratory apparatus, and the project has made significant progress in improving the predictive capability of models. The research will eventually determine how much methane can be displaced by a given amount of CO_2.

B.6.3 Physics and Chemistry of CO_2 Sequestration and CBM Production in Coal Seams

Pennsylvania State University is leading a research team on a project intended to provide guidelines for the drilling of new CBM production wells (NETL, 2002f). The results will enable field engineers to determine if cases of poor CO_2 sequestration and/or low methane production can be attributed to non-ideal coalbed temperatures and/or depths, or to other factors.

Thus far, the project has developed a method for simultaneously accounting for the heats and amounts of CO_2 and methane adsorption/desorption and the extents of dehydration. Mathematical methods for resolving complex temperature relationships have also been developed, and the researchers found an apparent correlation between hypothetical extents of coal dehydration and predicted relative viscosities of water in the narrow capillaries and pores of coal.

The project developed a laboratory system for the measurement of adsorption isotherms. The system was pressure-tested and successfully employed to generate data along with a derived equation used to separate the actual surface adsorption from the effects of coal swelling on the isotherm shape. The extent of actual physical adsorption was determined, the heats of adsorption were calculated, and the values were found to agree within 10 percent of each other. The project has resulted in the development of a new theory of coal swelling and how the CO_2 adsorption process affects swelling.

B.6.4 Geologic Screening Criteria for Sequestration of CO_2 in Coalbeds (Alabama)

The Geological Survey of Alabama and its partners are conducting research to determine the amount of CO_2 that can be stored in the Black Warrior basin of Alabama (NETL, 2002g). The CBM fairway of the Black Warrior basin is an excellent location to develop screening criteria and procedures. According to the EPA, Alabama ranks 9th nationally in CO_2 emission from power plants, and two coal-fired power plants are located within the CBM fairway. More than 34 billion cubic meters of CBM have been produced from the Black Warrior basin, which ranks second globally in CBM production. Production is now leveling off, and ECBM recovery has the potential to offset impending decline and extend the life and geographic extent of the fairway far beyond current projections.

The project will quantify CO_2 sequestration potential in Black Warrior CBM fairway, develop a screening model that has wide applicability, and apply the screening model to identify favorable demonstration sites for CO_2 sequestration. The partners have performed subsurface geological analyses and collected hydrologic and geothermic data from more than 2,800 well logs. Preliminary results confirm that coal can adsorb significantly more CO_2 than methane while having relatively little capacity to adsorb nitrogen.

B.6.5 Geologic Sequestration of CO_2 in Deep, Unmineable Coalbeds (New Mexico and Colorado)

Advanced Resources International (ARI) and its partners are using the only long-term, multi-well ECBM projects that currently exist in the world to evaluate the feasibility of storing CO_2 in deep, unmineable coal seams (NETL, 2003d). The two existing ECBM pilot sites are located in the San Juan Basin in northwest New Mexico and southwest Colorado. The knowledge gained studying these projects is being used to verify and validate gas storage mechanisms in coal seams, and to develop a screening model to assess CO_2 sequestration potential in other promising coal basins of the U.S.

Two field pilot sites, the Allison Unit (operated by Burlington Resources) and the Tiffany Unit (operated by BP Amoco), are demonstrating CO_2 and N_2 ECBM recovery technology, respectively. The interest in understanding how N_2 affects the process has important implications for power plant flue gas injection, because N_2 is the primary constituent of flue gas. As the current cost of separating CO_2 from flue gas is very high, this project is evaluating an alternative to separation by sequestering the entire flue gas stream. Another reason for considering CO_2/N_2 is that N_2 is also an effective methane displacer that can improve methane recoveries and further reduce the net cost of CO_2 sequestration. The Allison Unit pilot area, which has been in operation since 1995, includes 16 production wells and 4 injection wells. The Tiffany Unit pilot area, which has been in operation since 1998, consists of 34 production wells and 12 injection wells.

This demonstration project is providing valuable new information to improve the understanding of coal formation behavior with CO_2 injection, as well as the ability to predict results and optimize the process through modeling. The field studies have clearly demonstrated that ECBM via CO_2/N_2 injection and CO_2 sequestration in coal seams is technically feasible. A nationwide assessment indicates that this approach has the potential to sequester 90 billion metric tons of CO_2 and provide an additional 150 trillion cubic feet of gas supply for the U.S. Field and laboratory data have provided important new insights into the process, such as the tendency for coal to swell when it comes into contact with CO_2, which reduces permeability and injection rates. The research has also increased the understanding of processes for methane displacement by CO_2. These findings are being incorporated into a software model that can be used by industry to screen site-specific sequestration opportunities in coalbeds.

B.6.6 Sequestration of CO_2 in Unmineable Coal Seams with ECBM Recovery (West Virginia)

In another project sponsored by NETL, CONSOL Energy, Inc. will demonstrate a novel drilling and production process that reduces potential methane emissions from coal mining, produces usable methane, and creates a sequestration sink for CO_2 in unmineable coal seams (NETL, 2005a). CONSOL's project will employ a slant-hole drilling technique to drain CBM from a minable coal seam and an underlying unmineable coal seam. Upon drainage of 50 to 60 percent of the CBM, some of the wells will be used to inject and sequester CO_2 in the unmineable seam while stimulating additional methane production. The primary goal of this project is to evaluate the effectiveness and economics of carbon sequestration in an unmineable coal seam. Dewatering and degassing of wells have begun. The West Virginia Department of Environmental Protection has permitted the Central Well site's modified wells. The operators performed an environmental assessment under NEPA (NETL, 2002o) and DOE issued a Finding of No Significant Impact (FONSI).

B.7 ENHANCED OIL RECOVERY AND ENHANCED GAS RECOVERY

Current R&D projects and large-scale field tests are described in the following paragraphs.

B.7.1 The GEO-SEQ Project – Geological Sequestration of CO_2

A consortium of national laboratories is conducting the GEO-SEQ Project, including Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, and Oak Ridge National Laboratory, as well as educational institutions, and private industry firms (LBNL, 2004). The goals are to reduce the cost of sequestration, to develop a broad suite of sequestration options, and to ensure that long-term sequestration practices are effective and do not introduce new environmental problems. The project includes eight tasks intended to achieve these goals, including the Frio Test Well (see Section 3.2.2.3). With respect to EOR sequestration, the project seeks to develop methods for simultaneously optimizing sequestration of CO_2 in depleted oil and gas fields and increasing oil and gas production. Results will lay the groundwork for rapidly evaluating performance at candidate sequestration sites, as well as monitoring the performance of CO_2 in enhanced oil and gas recovery. The GEO-SEQ Project also includes tasks that are more closely associated with MM&V (see Section 3.2.3).

B.7.2 Weyburn CO_2 Sequestration Project (Canada)

The Weyburn oil field, located on the northwestern rim of the Williston Basin in the southern part of Saskatchewan Province, Canada, was first drilled in 1954. Today, about 650 production and water injection wells are operated by EnCana Resources (formerly PanCanadian Resources). During its lifetime, the 70-square mile oil field has produced some 55 million cubic meters of oil from primary and water-flood production. In October 2000, EnCana began EOR efforts using CO_2 to extend the life of the Weyburn field by more than 25 years, anticipating the extraction of 130 million barrels of oil, or more, from the depleted field. A daily supply of 2.7 million cubic meters of waste CO_2 (95 percent pure) has been supplied to the Weyburn oil field from the Great Plains Synfuels Company in Beulah, North Dakota. Since its inception, the original project sponsors have been joined by DOE, the European Union, the Alberta Government, the Japanese ENAA, and industrial sponsors, including BP, ChevronTexaco, TotalFinaElf, Dakota Gasification Co., TransAlta Utilities, SaskPower and Nexen. Now in its fifth year, the Weyburn Project represents a unique opportunity for these governments and industries to collaborate on the largest emissions-reduction project to date (Fitzpatrick, 2004 and NETL, 2004m).

Among its key aspects, the Weyburn Project is using waste CO_2 for a miscible flood EOR project and is studying the behavior of the CO_2 in the depleted oil field. Over the project's lifetime, approximately 20 MMT of CO_2 will be stored in the Weyburn oil field; recycling and eventually storing 0.3 percent of the world's total annual CO_2 emissions, which is an amount equivalent to emissions generated by the state of Maryland.

The Weyburn Project is attempting to answer questions that have not been considered in most EOR operations, such as what happens to the stored CO_2, how much can be stored, as well as the relative merits of storage with enhanced oil production. Researchers are gathering information before and after CO_2 flooding to assess the effectiveness of CO_2 as an EOR agent and to analyze the conditions and behavior of the CO_2 in the oil field. Another element of the study is determining yield and storage capacity to fully realize cost effectiveness, i.e., determining the potential CO_2 storage capacity of the reservoir for every enhanced barrel of oil produced.

Until now, vague knowledge of the geologic formation and activities, combined with the constant fluctuation of oil prices, has made predicting the economic success of EOR projects difficult. But the historical data on the Weyburn oil field is expected to provide unique insights for a sound economic model of current and future CO_2-EOR/sequestration efforts. The efforts of this and other EOR/sequestration projects are intended to give worldwide support to the notion that geologic storage is a safe, environmentally acceptable means of CO_2 mitigation.

The major permitting activity for this project is related to a nearly 200-mile pipeline needed to transport CO_2 from Dakota Gasification in the United States to the Weyburn field in Canada. After a public hearing, Canada's National Energy Board approved the application from Souris Valley Pipeline in October 1998. The Federal Energy Regulatory Commission approved the pipeline in the U.S., which travels west from Dakota Gasification and then north following oil reservoirs. This path took the pipeline through North Dakota's cherished badlands, which raised concerns about the land disturbance for the corridor. Basin Electric employees and others worked proactively to restore the land disturbed by the buried pipeline, in compliance with U.S. DOT rules. Also, Haines Construction Company, the pipeline contractor, used backhoes instead of a conventional trencher, which enabled topsoil to be separated and replaced on top. Six years later, the pipeline route is difficult to discern in many places during aerial surveys.

B.7.3 Sequestration of CO_2 in West Pearl Queen Field (New Mexico)

Sandia National Laboratory and Los Alamos National Laboratory have partnered with Strata Production Company to investigate downhole injection of CO_2 into a depleted oil reservoir, the West Pearl Queen Field in New Mexico (NETL, 2003e). This project is using a comprehensive suite of computer simulations, laboratory tests, and field measurements to understand, predict, and monitor the geochemical and hydrogeologic processes involved. The overall objective of this project is to better understand, predict, and monitor CO_2 sequestration in a depleted sandstone oil reservoir. Injection into this reservoir was through an inactive well, while a producing well and two shutoff wells are being used for monitoring. Approximately 2,100 tons of CO_2 - equivalent to one day's emissions from an average coal-fired power plant - have been injected into the formation. After the CO_2 has been allowed to "soak" into the reservoir rock, a second 3-D seismic survey will be taken. These observations will begin to tell scientists the fate of the CO_2 plume and will be used to calibrate, modify, and validate modeling and simulation tools. The project received a categorical exclusion under NEPA based on the fact that it was a small-scale, limited-duration injection deep underground.

B.7.4 In Salah Gas CO_2 Storage Project

In Salah Gas (ISG) is a joint venture project between BP, Statoil, and Sonatrach, involving a phased development of eight gas fields located in the Algeria Central Sahara, with a contracted sales gas stream of 9 billion m^3/year. These gas fields contain CO_2 concentrations ranging between 1 and 9%, which is above the export specification of 0.3%, therefore requiring CO_2 removal facilities. ISG has made a discretionary investment to enable compression and re-injection of the produced CO_2 gas stream, up to 70 MMscfd or 1.2 $MMTCO_2$, for geologic storage. Production operations and CO_2 re-injection began in

August 2004. The ISG project represents the first commercial scale injection of CO_2 into an active producing natural gas reservoir (Riddiford, et.al., 2005).

The storage scheme has the CO_2 re-injection directed into the aquifer region in the carboniferous reservoir, down-dip of the main hydrocarbon accumulation. To achieve a successful CO_2 injection scheme, a number of peripheral injection wells were required to mitigate potentially high injection pressures, access the peripheral reservoir volumes for sub-surface storage, and manage the placement of the injected CO_2. Effective placement of the CO_2 is important, with geosteering of the wells to target high porosity, high permeability intervals. It requires that the injected gas, which is driven by gravitational forces and the pressure sink associated with production, is retained within the aquifer zone and does not enter the main field area until after it has been depleted and abandoned. This is projected to be after 25 to 30 years of production.

The ISG project is expected to contribute to setting precedents for monitoring, regulation, and verification of geologic storage, and establish CO_2 capture and storage as eligible for GHG mitigation credits. Monitoring at In Salah Gas will serve a number of purposes:

- Enable optimization and management of hydrocarbon production (rates and reserves over time) by quantifying the impact of CO_2 re-injection and reducing uncertainties over time.
- Develop a detailed understanding of the behavior of the CO_2 storage with a view to reducing uncertainties in predictions of long-term storage performance.
- Test and demonstrate the technologies necessary for early detection of seepage of CO_2 out of the primary containment to enable intervention and maintain the integrity of long-term storage.

The project will require extensive monitoring of the storage site and overburden using a range of existing and novel technologies, including repeat 3D seismic, well-bore aquifer, and surface monitoring, plus extensive modeling of the whole system (Riddiford, et.al., 2005).

Examples of the MM&V technologies planned for implementation as part of the ISG joint industry program include the following (Wright, et.al., 2005):

- Sample analysis of water, gas, and solids
- Noble gas tracers injected with the CO_2
- Pressure surveys, surface and down-hole (static and interference)
- Electric logs (production, seismic profiles, and tomography)
- Gravity baseline, soil-gas survey, micro-seismic and tilt meters
- Meteorology and microbiology
- 4D seismic
- Aquifer monitoring well with oriented cap rock core and cuttings analysis
- Down-hole gravity and geo-mechanical monitoring
- Surface eddy flux co-variance data

B.8 SEQUESTRATION IN SALINE FORMATIONS

Current R&D projects and large-scale field tests are described in the following paragraphs.

B.8.1 Sleipner – The World's First Commercial-Scale CO_2 Capture and Storage Operation (Norway)

Statoil's Sleipner West Gas Field in the Norwegian North Sea is one of the world's largest producers of natural gas, but the produced gas (9 percent CO_2) does not meet end use or pipeline specifications. To reduce the CO_2 content to the 2.5 percent product specification level, while meeting Norwegian CO_2 emissions targets (a Norwegian CO_2 tax was instituted in 1995), a sequestration strategy was adopted in October 1996. Statoil manages the research at Sleipner, which is coordinated by the International Energy Agency's (IEA) Greenhouse Gas R&D Programme. DOE is a member of this IEA program. Other contributing partners include BP Amoco, ExxonMobil, Norsk Hydro, Saga, and Vattenfall. International government and industry organizations are providing research and technology.

In this project, unwanted CO_2 is stored 1,000 meters beneath the seabed in a saline formation. As a result of this CO_2 storage operation, Norway's CO_2 emissions are reduced by about 3 percent per year. Since the project's inception, 1 MMT of CO_2 have been stored each year, which is an amount equal to the CO_2 emissions of a typical 150 mega-watt (MW) coal-fired power plant located in the U. S.

Two towers, each about 20 meters high, are located on the Statoil North Sea platform. In the first tower, the CO_2 is captured by amine absorption and compressed. Energy freed during the amine process is used to run two 3 MW generators, thereby providing power for the platform. Next, the CO_2 is stripped from the amine, resulting in injection-ready CO_2. A separate injection well is used to inject the CO_2 into the Utsira aquifer, which is a massive saline sandstone formation with a shale caprock 1,000 meters under the seabed. The hydrocarbon reservoir used for natural gas production lies 3,500 meters below the seabed under the Utsira formation.

It is estimated that the Utsira formation can store up to 600 billion metric tons of CO_2. Hence, the total CO_2 emissions from all of Europe's power plants could be stored in this structure for the next 600 years. While permanent storage cannot be assured, it is estimated that the injected CO_2 will remain in the structure for at least the next several centuries.

B.8.2 Frio Formation Test Well (Texas)

In the first U.S. field test to investigate the ability of saline formations to store GHGs, the University of Texas at Austin is leading a team on a effort (NETL, 2004k) co-sponsored by NETL under the GEO-SEQ Project (see Section 3.2.2.2). The Frio Brine Pilot Experimental Site is located 30 miles northeast of Houston, in the South Liberty oilfield. The site is representative of a very large extent of the geology from coastal Alabama to Mexico, and will provide experience useful in planning CO_2 storage in high-permeability sediments worldwide. The subsurface geology of the region is well known. CO_2 has been successfully injected in the region for EOR, and fluid injection for waste disposal is widely practiced. However, modeling by Lawrence Berkeley National Laboratory (LBNL) has identified some poorly known variables that control CO_2 injection and post-injection migration.

The investigators performed an environmental assessment under NEPA (NETL, 2003m) and a FONSI was issued. As a part of a request for a Class V permit under the Underground Injection Control (UIC) program from the Texas Commission on Environmental Quality, the project developers prepared a high-quality 100-page document describing the geology and hydrology of the injection zone, plans for construction and operation of the injection well, and results from a reservoir modeling effort. The Class V permit request was based on the fact that the Frio area is primarily a depleted oil field, and that the current experiment would be conducted in a saline zone using an undisturbed geologic formation that would provide clearer data and enhanced knowledge. The Class V permit was granted by the state.

The team drilled a 5,753 foot injection well and developed a nearby observation well to study the ability of the high-porosity Frio sandstone formation to store CO_2. In October 2004, the researchers injected 1,600 tons of CO_2 into the formation over a 9-day period. The CO_2 was injected from 5,053 to 5,073 feet below the surface into the saline reservoir contained within a fault-bounded compartment covered by a 200-foot caprock of Anahuac shale.

A variety of methods are being used to monitor the movement of CO_2 in the formation. Before injection, baseline aqueous geochemistry, wire-line logging, cross-well seismic, cross-well electromagnetic imaging, and vertical seismic profiling - as well as two-well hydrologic testing, surface water, and gas monitoring- were completed. These monitoring efforts were repeated at intervals during the injection phase and are continuing with the objective of determining the stability of CO_2 storage in the formation.

Measurements made during this field test will help define the correct values for variables identified by LBNL, and will enable researchers to better conceptualize and calibrate models to plan, develop, and effectively monitor larger scale, longer timeframe injections. The researchers plan to perform follow-on testing with a larger volume of CO_2 and longer term monitoring to determine the formation's capacity to store CO_2 and to identify any potential environmental impacts.

B.8.3 An Investigation of Gas/Water/Rock Interactions and Chemistry

NETL and USGS are planning to lead an experimental study to assess the role of the chemistry of formation water in CO_2 solubility and the role of rock mineralogy in determining the potential for CO_2 sequestration through geochemical reactions (NETL, 2002i). The project would focus on the complex solution and surface chemistry of CO_2 in brines in the presence of host rock and the special types of analyses required to study the reaction kinetics. Carbonate mineral formation/dissolution reactions that may be important in geologic sequestration in deep saline formations will be identified. The kinetics of CO_2 dissolution in the liquid phase and subsequent substrate-water reactions are slow and poorly understood. Therefore, understanding the kinetics of both types of reactions and the processes controlling them is essential to understanding the conversion of CO_2 into stable carbonate minerals.

A compilation of existing brine data from a variety of sources, and a complete statistical analysis of the brine chemistry and other geological parameters associated with saline formations, will be a valuable tool for both experimental and modeling studies of CO_2 sequestration in brines. Currently, NETL is developing a brine database that includes temperature, depth, pressure, and a variety of chemical variables (pH, sodium, iron, chloride, bicarbonate, calcium, magnesium, sulfate, and total dissolved solids) on some 64,000 brines taken from the contiguous U.S. Sources of these data include those provided by the USGS, searches of geoscience literature, state geological surveys, and oil and gas producing companies. Additionally, NETL has instituted a limited field program of brine collection throughout the U.S. This brine sampling is being done in conjunction with other government agencies and oil and gas companies.

B.8.4 Optimal Geological Environments for CO_2 Disposal in Saline Formations in the U.S.

The Bureau of Economic Geology, University of Texas at Austin, is developing criteria to characterize optimal conditions and characteristics of saline formations that can be used for long-term storage of CO_2 (NETL, 2002j). Phase I of this project included identifying drilling locations for CO_2 injection wells and better defining saline formation conditions suitable for CO_2 disposal and sequestration. During Phase II, saline water-bearing formations outside of oil and gas fields were investigated.

Recent R&D efforts have demonstrated the technical feasibility of the process, defined costs, and modeled technology needed to sequester CO_2 in saline formations. One of the simplifying assumptions used in previous modeling efforts is the effect of stratigraphic complexity on transport and trapping in saline formations. Phase III efforts will include field testing of a limited amount of CO_2 injected into a deep saline reservoir within the state of Texas to ascertain the interaction of the gas with the reservoir rock and to monitor the size and shape of the CO_2 plume within the reservoir. Current effort is directed at a field test of injecting a set amount of CO_2 into a deep saline reservoir and monitoring the interaction of the gas with the reservoir and the dispersion of the CO_2 with time.

This project will benefit industry by extending modeling and monitoring capabilities for sequestration into the geologic settings where very large-scale sequestration is feasible in the geographic areas where sequestration is needed. Nonproductive brine-bearing formations below and hydrologically separated from potable water aquifers have been widely recognized as having high potential for very long term (geologic time scale) sequestration of GHGs, and this site will provide a first field-scale testing in this setting. It will also provide a regional U.S. data inventory of saline water-bearing formations.

B.8.5 Chemical Sequestration of CO_2 in Deep Saline Formations in the Midwest United States

Battelle Memorial Institute is leading a consortium of industries and institutions sponsored by NETL in a field study to determine whether the deep rock layers in the Ohio River Valley are suitable for storing CO_2 (NETL, 2003f). The Ohio River Valley is home to the largest concentration of fossil fuel fired electricity generation in the nation. American Electric Power (AEP) owns and operates the Mountaineer Power Plant, which is the host site for the research project. The project involves site assessment to develop the baseline information necessary to make decisions about a potential CO_2 geologic disposal field test and verification experiment at the site. Additionally, the potential for long-term sequestration of CO_2 in deep, regional sandstone formations and the integrity of overlying caprock will be evaluated for future sequestration projects.

Regional-scale assessments in the Midwest and other regions show that there is enormous potential sequestration capacity in sedimentary basins with favorable formation thickness, hydrogeology, seismicity, and proximity to CO_2 sources. However, site-specific tests and characterization are needed to determined injection potential at individual locations. The project is currently in Phase III, which is focused on a site characterization (surface and subsurface) for possible injection of CO_2 into a suitable formation. CO_2 injection is not planned during this phase. However, if studies show that storing CO_2 deep underground in the Ohio River Valley will be safe, practicable, and effective, AEP and its partners will decide whether to go to the next stage, involving active CO_2 injection.

B.8.6 Pioneer Project, American Electric Power (AEP)

AEP is also exploring the possibility of capturing CO2 from its Pioneer Power Plant in New Haven, West Virginia and injecting it into a saline reservoir that underlies the facility. The project is currently in the assessment phase, and CO_2 has not yet been injected. AEP has performed preliminary designs of CO_2 capture and onsite pipeline transport to ensure they do not violate any of the facility's existing permits. Seismic tests of the region have been conducted and a 10,000-foot test well was drilled. These activities were granted a categorical exclusion under NEPA on the basis that they were necessary to acquire data to perform an Environmental Assessment. The West Virginia State Oil and Gas Division granted the well a test well variance under the UIC Program. AEP has undertaken a significant community outreach and education effort in preparation for possible future CO_2 injection.

B.8.7 Reactive, Multiphase Behavior of CO_2 in Saline Formations Beneath the Colorado Plateau

The University of Utah is leading an effort to conduct an in-depth study of deep saline reservoirs in the Colorado Plateau and Rocky Mountain region (NETL, 2002h). These formations serve as natural analogs for CO_2 sequestration in saline formations, and can provide useful data to verify computer models. Small amounts of natural leakage from these reservoirs is occurring, and studying these leaks can provide insight into the environmental problems caused by leaks, the circumstances under which leaks can occur, and how problems can be mitigated. The project also provides for numerical simulation of CO_2 sequestration in these formations, including reactive modeling for chemical reactions between the rocks in the formation and CO_2 (Klara, et al., 2003). The study will enable researchers to determine how much CO_2 can be stored, what happens to the stored gas, and the long-term environmental risks associated with storage.

B.8.8 New Techniques for Injecting CO_2 into Saline Formations

Texas Tech is performing a project sponsored by NETL (Klara, et al., 2003) to develop a well-logging technique to characterize geologic formations, including the quality and integrity of caprock, using nuclear magnetic resonance (NMR). The use of NMR precludes the need for core sampling, and can be performed more quickly and efficiently. The research is directed at identifying suitable sites for CO_2 injection at which controlled hydraulic fracturing can be used to create artificial zones of high permeability. Such actions could significantly reduce the number of wells required for injection.

B.9 SEQUESTRATION IN OTHER NOVEL GEOLOGIC FORMATIONS

Promising but untested reservoir types have significant carbon storage capacity and the potential for value-added hydrocarbon production with CO_2 storage.

B.9.1 Analyses of Devonian Black Shales in Kentucky for Potential CO_2 Sequestration

A project led by the University of Kentucky is investigating the untested concept that black, organic-rich Devonian shales, like coals, could serve as significant geologic sinks for CO_2 (Nuttall, 2004). Devonian shales underlie approximately two-thirds of Kentucky. In these shale formations, natural gas is adsorbed on clay and kerogen surfaces, analogous to methane storage in coalbeds. It has been demonstrated in gassy coal that, on average, CO_2 is preferentially adsorbed, displacing methane at a ratio of 2 for 1. It is believed that black shales may similarly desorb methane in the presence of CO_2.

For this project, drill cuttings from the Kentucky Geological Survey Well Sample and Core Library are being sampled to collect CO_2 adsorption isotherms. Sidewall core samples have been acquired to investigate CO_2 displacement of methane, and an elemental capture spectroscopy log has been acquired to investigate possible correlations between adsorption capacity and mineralogy. The study has shown that CO_2 adsorption capacities at 400 psi range from a low of 19 scf/ton in less organic-rich zones to more than 86 scf/ton in the Lower Huron Member of the shale.

It has been estimated, based on these data, that the Lower Huron Member of the Ohio Shale of eastern Kentucky has the capacity to sequester 5.3 billion tons of CO_2 and that the deeper Devonian shales in Kentucky may hold up to 28 billion tons. If the black shales of Kentucky are shown to be a feasible geologic sink for CO2, their widespread distribution in the Paleozoic basins throughout North America should make them an attractive location for CO_2 storage and enhanced natural gas production (Nutall, 2004).

B.9.2 Sequestration Potential of Texas Low-rank Coals

The Texas Engineering Experiment Station of Texas A&M University is leading a project to investigate the technical and economic viability of CO_2 sequestration in Texas' low-rank coals, and the potential for enhanced CBM recovery (NETL, 2004c). The study will include an analysis of the volumes and composition of Texas power plant flue gases, the detailed characterization of prospective coalbeds, and computer simulation of CO_2 sequestration in the coals.

B.9.3 CO_2 Sequestration in Carbonate Sediments Below the Sea Floor

In a project awarded by NETL in 2004, scientists from Harvard University, Columbia University, Carnegie Mellon University, and the University of California at Santa Cruz will investigate the feasibility of sequestering CO_2 by injecting it below the sea floor in calcium carbonate sediments (NETL, 2004l). These sediments could act as absorbents for the CO_2, but they warrant study because the chemistry, temperature, and pressure below the sea floor are different than in underground sequestration on land. The experiments will use pressurized tanks in a laboratory as a modeling tool to simulate the conditions below the sea floor. The researchers will seek to understand the mechanical and chemical behavior of CO_2 and CO_2/ H_2O mixtures injected into carbonate sediments under a range of pressures and temperatures, and with a range of sediment compositions.

B.9.4 CO_2 Sequestration in Redbed Sandstones

In another project awarded by NETL in 2004, scientists at the University of Pittsburgh will attempt to store CO_2 with SO_2 in redbed sandstones containing feldspar and iron oxides (NETL, 2004l). This project will incorporate modeling and bench-scale testing and will study geological sequestration of CO_2 using the carbonation process. The researchers will use an electron microscope to evaluate reactions that occur at the molecular and atomic levels, and they will try to determine what happens when CO_2 and the minerals interact. They intend to determine whether iron carbonates will form, whether the porosity of the minerals will change, and whether CO_2 will leak out over a large area after many years of storage.

B.9.5 Enhancing Carbonation in Underground CO_2 Sequestration

Yet another project awarded by NETL in 2004 will study the chemistry and kinetics of carbonation using commonly occurring minerals (e.g., olivine) as the geochemical method for sequestering CO_2 (NETL, 2004l). This project, to be conducted by researchers at the Center for Solid State Science at Arizona State University, will use sonic frequencies to increase the exfoliation and particle cracking of the minerals to enhance CO_2 sequestration. Through modeling and experimental investigations, the scientists will attempt to speed up, control, and tailor the carbonation process. As the result of this research, the scientists intend to discover whether CO_2 can be sequestered permanently underground in this manner.

B.10 TERRESTRIAL SEQUESTRATION

Current projects, some of which are summarized in the following paragraphs, include a large-scale demonstration of reforesting recently mined lands in Kentucky and Virginia and a smaller-scale demonstration integrating terrestrial sequestration with the energy production by employing the use of coal combustion byproducts. These projects are based on fostering partnerships between landowners, biomass and biofuels industry representatives, government agencies, and energy producers.

B.10.1 Enhancement of Terrestrial Carbon Sinks through Reclamation of Abandoned Mine Lands in the Appalachians

Stephen F. Austin State University (SFASU), working with Texas Utilities and Westvaco, is studying the CO_2 sequestration potential resulting from afforestation of abandoned mined lands using Northern red oak (NETL, 2003h). Within the Appalachian coal region, there may be up to 400,000 hectares of abandoned mined lands. These areas contain little or no vegetation, provide little wildlife habitat, and may pollute streams. Reclamation and afforestation of these sites has the potential to sequester large quantities of carbon in terrestrial ecosystems. Utility companies with high CO_2 emissions are interested in mitigating these emissions through the use of carbon credits. In order to establish a carbon credit market and claim carbon credits, utility companies need to partner with landowners who do not currently have forests on their land. Abandoned mined lands in Appalachia can offer excellent sites for such partnerships.

This project will determine how to increase carbon sequestration in forests while increasing forest yields and providing other desirable ecosystem benefits. Growth and yield models will be applied to commercial tree species in order to quantify the maximum amount of carbon that can be stored. Discounted cash-flow analyses will be conducted and the soil expectation value will be calculated to predict the per ton cost of carbon sequestration. A carbon credit market between landowners, utility and coal companies will be investigated, as well as analysis of the impact of sequestration on the local economy.

B.10.2 Enhancing Carbon Sequestration by Matching Amendment Techniques and Land Types

Oak Ridge National Laboratory and Pacific Northwest National Laboratory are leading a project to determine the best way to increase the carbon sequestration potential of land previously disturbed by mining, highway construction, or poor land management practices (NETL, 2003g). The team will focus on the use of amendments derived from paper production, biological waste treatment facilities, and solid byproducts from fossil-fuel combustion to identify and quantify the key factors necessary for the successful reclamation of degraded lands. The results will be summarized in a set of guidelines containing practical information about matching amendment combinations to land types and optimum site-management practices. Long-term field studies will be designed and sites recommended for demonstration and further optimization.

B.10.3 Carbon Capture and Water Emissions Treatment System at Fossil-fueled Electric Generating Plants

The Tennessee Valley Authority (TVA) and Electric Power Research Institute (EPRI) have partnered on an effort to demonstrate and assess the life-cycle costs of integrating electricity production with enhanced terrestrial carbon sequestration (NETL, 2002k). The project is being conducted on coalmine spoil land at the 2,558 MW Paradise Station in Kentucky. This station, which burns bituminous coal and is currently equipped with flue gas desulfurization (FGD) for SO_2 control and is set to begin using selective catalytic reduction for NO_X control, will use the byproducts from these control systems to amend the mine soils. Treated water from the FGD system settling pond discharge will be used to irrigate the soils. Benefits include the use of byproducts to improve reclamation sites and enhance carbon sequestration, the development of a passive technology for the reduction of criteria pollutant release to water, the development of wildlife habitat and green space, the generation of Total Maximum Daily Load (TMDL) credits for water and airborne nitrogen, and the development of additional forestlands. After 2 years the planted trees will have demonstrated greater than 80 percent survival rates and have the potential to sequester carbon at rates up to 6.7 metric tons per hectare per year.

B.10.4 Actively Mined Land Reclamation in Kentucky

The University of Kentucky is leading an effort to study the use of low-compaction reclamation techniques to facilitate reforestation (NETL, 2005a). More than 550 acres of mined land have been planted with high value hardwoods. Each site has been prepared using the FRA by either ripping previously mined sites or loosely compacting new soils that will act as a rooting medium. The research effort will consider the effect of species, spoil type and spoil handling on carbon sequestration. An economic assessment will be completed to determine the cost and potential to reclaim previously mined lands.

B.10.5 Restoring Sustainable Forests on Appalachian Mined Lands in West Virginia and Virginia

Virginia Tech is leading a project to demonstrate terrestrial sequestration for wood products, renewable energy, carbon storage, and other ecosystem services on three 30- to 40-hectare strip mine areas owned by Mead-Westvaco Corporation and Plum Creek Timber Company in West Virginia and Pittston Coal Company in Virginia (NETL, 2003h). The project intends to determine mine soil properties that influence the amount of carbon sequestered. Terrestrial sequestration testing will determine the biological and economic potential of reforesting the sites. Cost-benefit analyses will be done for each management approach. Thus far, a carbon inventory has been made for 14 mined and 7 non-mined forests across an age and site quality gradient. Trees were planted in March 2004 on the study sites and an intensive measurement and monitoring program is underway to estimate the carbon sequestration potential at the sites (NETL, 2003h).

B.10.6 Exploring Terrestrial Sequestration Opportunities in the Southwest United States

The Applied Terrestrial Sequestration Partnership, an integrated research program led by Los Alamos National Laboratory (LANL) and NETL, is taking a leading role in developing breakthrough technologies and applications for terrestrial carbon sequestration (NETL, 2003g). Understanding both ecosystem dynamics and economic issues is critical to the success of terrestrial sequestration as a policy option. Marginal lands (forest, farm, range, or industrial) can serve as a barometer for climate change and are ideal field sites for investigating terrestrial sequestration. The study uses a multidisciplinary approach, integrating lab and field studies with modeling (using CENTURY algorithms). The results will provide a fundamental understanding of how changes in the plant community are reflected in carbon inventories and include a detailed economic analysis of carbon sequestration in reclamation sites.

B.10.7 Development and Application of Appropriate Tools and Technologies for Cost-effective Carbon Sequestration

The Nature Conservancy (TNC) is working in close collaboration with U.S. companies (including General Motors and American Electric Power), foreign governments, and NGO partners to develop a system of project planning tools and measurement technologies that can measure the carbon sequestration benefits on several existing carbon sequestration projects. The project is using new aerial and satellite based technology to study forestry projects in Brazil and Belize to measure the rate of change of carbon in aboveground biomass. Soil carbon technologies and sampling strategies are being developed to estimate the cost of determining the rate of change in soil carbon. Several software models are being applied or developed to determine: optimal land management practices; and locations where carbon benefits will be permanent and provide other benefits such as enhancing biodiversity. In addition, feasibility assessments are being conducted for ecosystems across the U.S. to determine the bio-physical and economic potential for carbon sequestration (NETL, 2003g).

B.11 OCEAN FERTILIZATION

Oceans absorb, release, and store large amounts of CO_2 from the atmosphere through natural processes. Ocean fertilization is one of two approaches for enhancing oceanic carbon sequestration that take advantage of the ocean's natural processes. This approach intends to enhance the productivity of ocean biological systems through fertilization or other means. The other approach, which involves injecting CO_2 into the deep ocean, is described in the next section.

Experimental results and observed surges in phytoplankton growth after dust clouds pass over certain ocean regions indicate that increasing the concentration of iron and other macronutrients in some ocean waters can greatly enhance the growth of phytoplankton and resulting CO_2 uptake. However, ocean fertilization remains highly controversial because of uncertainty surrounding other changes it may cause in complex marine environments (NETL, 2005b). Although there are no current R&D efforts underway for ocean fertilization in the Carbon Sequestration Program, future research in the following areas would be necessary to assess the feasibility of this approach:

- Establishing the scientific knowledge base needed to understand, assess, and optimize ocean fertilization;
- Developing effective macronutrient seeding methodologies; and
- Assessing the long-term fate and flux of CO_2 in marine environments.

B.12 DEEP OCEAN INJECTION OF CO_2

The world’s oceans represent the largest potential sink for CO_2 produced by human activities, but the scientific knowledge to support active ocean sequestration is not yet adequate. Oceans already contain the equivalent of an estimated 140 trillion tons of CO_2. Natural carbon transfer processes in oceans span thousands of years and will eventually transfer 80 to 90 percent of today’s manmade CO_2 emissions to the deep ocean. This natural CO_2 transfer may already be adversely affecting marine life and may also be altering deep ocean circulation patterns (NETL, 2002l).

Compared to terrestrial and geologic sequestration, the concept of ocean sequestration is in a much earlier stage of development. No commercial-scale applications of deep ocean injection have yet been conducted, although the Program has sponsored small-scale experiments. Research is focused on learning more about the ocean carbon cycle and deep ocean ecosystems, assessing the environmental impacts of CO_2 storage, and understanding the mechanisms by which CO_2 hydrates form. The Program previously funded laboratory experiments aimed at learning more about the basics of CO_2 drop behavior in an ocean environment and the behavior of CO_2 hydrates. NETL has the capability to simulate deep ocean conditions and has been conducting experiments on CO_2 droplet stability. Also, a conceptual design of infrastructure for CO_2 transport and injection has been developed (NETL, 2005b). Examples of current R&D projects are described in the following paragraphs.

B.12.1 Experiments on the Ocean Disposal of Fossil Fuel CO_2

Monterey Bay Aquarium Research Institute (MBARI) is leading a project sponsored by NETL to use a remotely operated vehicle (ROV) to carry out pilot experiments involving the deployment of small quantities of liquid CO_2 in the deep ocean (NETL, 2002l and 2005b). The project will investigate the fundamental science underlying concepts of ocean CO_2 sequestration. Below a depth of about 10,000 feet the density of liquid CO_2 exceeds that of seawater, and the liquid CO_2 is quickly converted into a solid clathrate hydrate by reacting with the surrounding water. Clathrate hydrates are a class of solids in which gas molecules are bound inside cages made up of hydrogen-bonded water molecules.

B.12.2 Optimized In Situ Raman Spectroscopy on the Sea Floor and Effects of Clathrate Hydrates on Sediment

In another project sponsored by NETL, a research group at Washington University in St. Louis will work with MBARI to carry out the first direct in situ analysis on the ocean floor of CO_2 clathrate hydrates, surrounding fluids, and sediments adjacent to the hydrates using a Raman spectrometer (NETL, 2002l). This information on the physical chemistry of clathrate hydrates and sediment interaction is essential for the evaluation of impacts of CO_2 ocean sequestration on the ocean floor ecosystem.

B.12.3 Accelerated Carbonated Dissolution as a CO_2 Capture and Sequestration Strategy

Lawrence Livermore National Laboratory and USGS are conducting laboratory studies to synthesize and investigate the physical properties of CO_2 hydrates and to contrast them with properties of methane hydrates (NETL, 2002l). Additionally, gas-solid exchange experiments will be performed with methane hydrates to determine whether methane extraction and CO_2 sequestration can be accomplished in a single step by replacing methane hydrates with CO_2 hydrates.

A related effort lead by the University of Pittsburgh is directed at determining the fate of CO_2 introduced into the deep ocean and how the icelike CO_2 hydrate impacts the process (NETL, 2002m). The experimental work is carried out in two facilities: a High-pressure, Variable-volume View-Cell (HVVC) and a High-pressure Water Tunnel Facility (HTWF). In addition, a Low-pressure Water Tunnel Facility (LWTF) capable of being chilled has been constructed and used to test various configurations of flow conditioners and section divergence angle and length. Results show that under conditions of temperature and pressure planned for deep-ocean sequestration, the formation of hydrate from dissolved CO_2 may be in areas of elevated dissolved CO_2 concentration, such as near the injection site. The project will provide useful information and models for the development and optimization of CO_2 storage in oceans.

B.12.4 Large Scale CO_2 Transportation and Deep Ocean Sequestration

The objective of a project led by McDermott Technology Inc. and the University of Hawaii is to investigate the technical and economic feasibility of large-scale CO_2 transportation and deep ocean sequestration by focusing on two cases. One case would involve ocean tanker transport of liquid CO_2 to an off-shore floating platform on a barge where it would be injected vertically to the ocean floor. The other case would involve transporting liquid CO_2 through undersea pipelines to the ocean floor (NETL, 2002l).

B.12.5 Collaboration with the International Project on CO_2 Ocean Sequestration

Several efforts sponsored by NETL have supported the International Project on CO_2 Ocean Sequestration (IPCOS), which involves four nations (United States, Japan, Norway, and Canada) and one private corporation (CABB of Switzerland). It includes field experiments at Keahole Point on the Kana Coast off the big island of Hawaii (NETL, 2002l and 2005b). One of NETL's projects has developed instrumentation and potential experiments for the IPCOS. Another NETL project has provided logistical and technical support for the IPCOS, including a surface vessel for the project, biological experiments, and a survey of potential test sites. Another project sponsored by NETL has conducted public outreach and permitting activities associated with the IPCOS. DOE also prepared an EA (NETL, 2001) to analyze the potential environmental impacts of an experiment to test the dissolution and dispersion of liquid carbon dioxide in ocean water at moderate depth, which concluded with the issuance of a FONSI.

B.13 GEOLOGIC SEQUESTRATION MONITORING, MITIGATION AND VERIFICATION (MM&V)

B.13.1 Weyburn Sequestration Project – Geologic Reservoir Mapping and Assessment

In the ongoing Weyburn Sequestration Project for EOR and geologic storage of CO_2 (see Section 3.2.2.2), new reservoir mapping and predictive tools are being used to develop a better understanding of the behavior of CO_2 in a geologic formation (NETL 2004m and 2005b). Key objectives of this research are to study the geological, geophysical and geochemical aspects of the Weyburn field and map the migration and distribution of existing formation fluids (including resident CO_2) as well as injected fluids. The goal of this effort is to measure and study the movement of the injected CO_2 at the Weyburn field and thereby expand the knowledge base of the capacity, transport, fate and storage integrity of CO_2 injected into geologic formations.

What has made the Weyburn oil field a most promising site for research is the Saskatchewan Province's near-complete collection of records and reports on the geophysical, production, and injection activities in CO_2 recycle compressors used in EOR activities at the Weyburn oil field since its discovery. These records are expected to provide a sound basis for developing analytical and monitoring methodologies for future carbon sequestration efforts (Fitzpatrick, 2004). By undertaking such monitoring projects and by demonstrating that the injected CO_2 can be stored effectively over geologic timescales, confidence will be enhanced in geologic storage as a CO_2 mitigation option.

B.13.2 Saline Formation CO_2 Storage (SACS) Project and MM&V Research at Sleipner

In conjunction with the sequestration project at the Sleipner West Gas Field in the Norwegian North Sea (see Section 3.2.2.2), the Saline Aquifer CO_2 Storage (SACS) project was initiated in 1997 to monitor and verify the fate of injected CO_2. The first phase of monitoring was completed in 2000, and researchers confirmed that there was no leakage from the Utsira formation. The spread of CO_2 through the formation is recorded by seismic surveys. SACS researchers are now developing methods and documentation to verify the reliability, environmental acceptability, and safety of CO_2 storage in saline reservoirs.

B.13.3 Sea Floor Gravity Survey of the Sleipner Field to Monitor CO_2 Migration

In a SACS-associated project sponsored by NETL, the Scripps Institute of Oceanography at the University of California, San Diego and Statoil are collaborating on a seafloor gravity survey to monitor CO_2 migration at the Sleipner site (NETL, 2004n). Utilizing high precision gravitational surveying techniques along with seismic data, the primary project goal is to quantify the change in the local gravitational field associated with the sequestration of CO_2 in the Utsira saline reservoir below the bed of the North Sea. This research will determine the effectiveness of using microgravity techniques to monitor and predict the behavior of geologically sequestered CO_2.

B.13.4 GEO-SEQ Project MM&V

The GEO-SEQ Project (see Section 3.2.2.2) has carried out eight separate, but related, tasks that provide new methods and approaches for reducing the cost and risk of geologic sequestration (NETL, 2004j). The results from these tasks will provide the basis for the development of a set of best practices for MM&V of geologic sequestration. The benefits of this project are anticipated to include lower sequestration costs, lower sequestration risk, decreased implementation time, and increased public acceptance. The eight tasks included in this project are:

- Co-optimization of carbon sequestration with oil and gas recovery
- Carbon sequestration with enhanced gas recovery
- Co-disposal of CO_2, H_2S, NO_X, and SO_2
- Evaluation of geophysical monitoring technologies
- Application of natural and introduced tracers
- Enhancement of numerical simulators for GHG sequestration in deep unminable coal seams and in oil, gas, and brine formations
- Improving the methodology for capacity assessment
- Frio pilot test.

As a component of the GEO-SEQ Project, the research team is seeking to provide methods that utilize the power of natural and introduced tracers to decipher the fate and transport of CO_2 injected into the subsurface. The team is investigating the effectiveness of tracers of stable isotopes (oxygen, sulfur, carbon, nitrogen), noble gas isotopes, and radioactive isotopes. The resulting data will be used to calibrate and validate predictive models used for: (1) estimating CO_2 residence time, reservoir storage capacity, and storage mechanisms; (2) testing injection scenarios for process optimization; and (3) assessing the potential leakage of CO_2 from the reservoir (NETL, 2005b).

B.13.5 Natural Analogs for Geologic CO_2 Sequestration (NACS)

Brookhaven National Laboratory is collaborating with LANL and other institutions on a MM&V project sponsored by NETL at the West Pearl Queen Oil Field (see Section 3.2.2.2) in New Mexico. The primary objective is to evaluate a wide range of surface and near-surface monitoring techniques that show promise in the detection of both the short term, rapid loss, and long-term, intermittent slow leakage of CO_2 from geologic formations (NETL, 2002n). The researchers are monitoring for CO_2 leakage at the West Pearl Queen site to determine the migration and fate of CO_2 after being injected into a depleted oil reservoir. Models and data developed will be used to predict physical and chemical changes in oil reservoir properties and the long-term storage capacity, safety, and integrity of oil reservoir sequestration.

The researchers have conducted background studies of geologic features, soil and atmosphere hydrocarbon patterns and concentrations, and selected monitoring locations and grid patterns for soil-gas sampling. They are using perfluorocarbon tracer compounds and evaluating tracer retention on coal. They are also performing geophysical site analysis from remote sensing and ground-based measurements by combining satellite visible and infrared views with satellite radar and optical aerial photography.

Natural Analogs for Geologic CO_2 Sequestration (NACS)

Advanced Resources International is leading a study sponsored by NETL to document the capability of depleted oil and gas fields to sequester CO_2 safely and securely (NETL, 2003i). The study will also investigate long-term reactions between CO_2 and the various minerals in the reservoir and cap rocks.

At present, five large natural CO_2 reservoirs in the United States provide a total of 25 million tons of CO_2 that is injected into oil fields for EOR. The NACS project is performing a multi-disciplinary geologic engineering study of three of these reservoirs (Kinder Morgan's McElmo field in Colorado, Ridgeway's St. Johns Dome in Arizona and New Mexico, and Denbury Resources' Jackson Dome field in Mississippi), with the objective of comparing the capabilities of naturally occurring CO_2 reservoirs with the capabilities of depleted oil and gas fields to sequester CO_2 securely and economically.

B.13.6 Depleted Oil Reservoir Migration

As a component of the West Pearl Queen Field sequestration project (see Section 3.2.2.2), the research team is using a comprehensive suite of computer simulations, laboratory tests, and field measurements to understand, predict, and monitor the geochemical and hydrogeologic processes involved during CO_2 sequestration in a depleted sandstone oil reservoir (NETL, 2003e). The project includes geologic flow/reaction modeling; geophysical monitoring of the advancing CO_2 plume; and laboratory experiments to measure reservoir changes due to CO_2 flooding. The models and data are being used to predict storage capacity as well as physical and chemical changes in reservoir properties, such as fluid composition, porosity, permeability, and phase relations.

B.13.7 Digital Spatial Database to Catalogue Geologic Sequestration Sites in the Midwest

The Mid-continent Interactive Digital Carbon Atlas and Relational Database (MIDCARB) is a joint project between the State Geological Surveys of Illinois, Indiana, Kansas, Kentucky, and Ohio, sponsored by NETL (NETL, 2003j). The purpose of MIDCARB is to enable the evaluation of carbon sequestration potential in the sponsoring states. When completed, the digital spatial database will allow users to estimate the amount of CO_2 emitted by sources (such as power plants, refineries and other fossil fuel consuming industries) in relation to geologic reservoirs that can provide safe, secure sequestration sites over long periods of time. MIDCARB is organizing and enhancing the critical information about CO_2 sources and developing the technology needed to access, query, model, analyze, display, and distribute natural-resource data related to carbon management.

B.13.8 Development of a Carbon Management Geographic Information System for the United States

The Massachusetts Institute of Technology (MIT) is leading a study sponsored by NETL to develop a systems analysis tool that will aid in the development and deployment of carbon capture and sequestration technologies in the U.S. (NETL, 2005b). This project will take a top-down approach to potential CO_2

sequestration storage sites and complement the MIDCARB project, which is using a bottoms-up approach in five Midwest states.

B.14 TERRESTRIAL SEQUESTRATION MM&V

B.14.1 Appropriate Tools and Technologies for Cost-effective Terrestrial Sequestration

Through the ongoing development and implementation of carbon sequestration projects on a demonstration scale, TNC is participating in a cooperative agreement with NETL to explore the compatibility of carbon sequestration in terrestrial ecosystems with the conservation of biodiversity (NETL, 2003k). TNC's first involvement in assessing this approach occurred in 1994 with the development of the Rio Bravo Carbon Sequestration Pilot Project in Belize. Since then, TNC has initiated several other projects with a variety of partners.

The collaborative effort with NETL is focused on gaining cost-effective, verifiable measurements of the long-term potential of various terrestrial carbon sequestration strategies and assessing land use practices that avoid emissions of CO_2. The project will use newly developed aerial and satellite-based technology to study forestry projects in Brazil and Belize to determine their potential for carbon sequestration, and it will also test new software models to predict how soil and vegetation store carbon at sites in the U.S. and abroad. The following are accomplishments to date:

- Advanced videography has been applied to pine savannah analysis in Belize.
- Feasibility studies on several different U.S. ecosystems have been initiated to determine which ecosystem types offer viable options for carbon sequestration.
- The GEOMOD spatial analysis tool has been used to determine and validate baseline analyses.
- An alternative baseline method developed by TNC (the Euclidean Distance between Agriculture and Forest (EDAF) method) has been further refined in baseline analyses in Brazil.
- A technical advisory panel was organized to address the issues associated with baseline and leakage estimates.
- Soil monitoring is being conducted using laser-induced breakdown spectroscopy (LIBS), which is being developed by the Los Alamos National Laboratory.

B.14.2 Next-Generation Soil Carbon Measurement

The LANL and USDA are collaborating on the development of an advanced Laser-Induced Breakdown Spectroscopy (LIBS) device for field-based detection of soil carbon. The goal is a LIBS device that will enable researchers to obtain accurate measurements of soil carbon in several seconds (NETL, 2005b).

B.14.3 Genetic Diversity Analyses as an Indicator of Soil Carbon Accumulation

The LANL is leading an effort to develop a better understanding of plant growth and relationships between carbon storage, soil microbes, and water and nutrient utilization. Studies are directed at advanced plant growth, soil microbes and carbon/water interactions to enhance vegetation growth to maximize carbon storage, evaluating carbon transfer from plant to soil, and assessing and improving land management practices to increase net carbon storage (NETL, 2005b).

B.14.4 Ocean Sequestration MM&V

Established protocols for measuring dissolved organic and inorganic carbon in ocean waters have been developed as a part of varied studies of ocean ecosystems. Additional research is needed to provide a capability to visualize hydrate formation, as well as to develop advanced tools (e.g., diffraction, nuclear magnetic resonance spectroscopy, and Raman spectroscopy) for monitoring seawater chemistry and biological impacts in situ (NETL, 2005b).

B.15 BREAKTHROUGH CONCEPTS

An alternative to sequestering CO_2 as a gas, liquid, or solid is to convert it into another chemical compound. Many CO_2 conversion processes are found in nature, the most common of which is photosynthesis. Additionally, mollusks and crustaceans use CO_2 that is dissolved in ocean water to build their carbonate-based shells. Sandstone also reacts with CO_2 in the air to form minerals. Further evidence suggests that CO_2 trapped in geologic formations over eons has been converted to methane, carbonates, and other compounds though biochemical processes (NETL, 2005b).

The Carbon Sequestration Program seeks to mimic naturally occurring processes when developing breakthrough CO_2 conversion methods. This is a challenging task, because CO_2 is a highly stable compound containing a very low amount of chemical energy, and the natural conversion processes are slow and inefficient as a consequence. The Program is performing applied research to complement the efforts of organizations conducting basic scientific research in this field, including research by the DOE Office of Science and the National Science Foundation.

The CO_2 conversion processes can reduce net carbon emissions and provide significant secondary benefits such as the following:

- Photosynthesis and other biochemical processes convert CO_2 into fuel (biomass), creating regenerable energy systems that can displace new fossil resource use.
- Certain biochemical processes use CO_2 to produce pharmaceutical compounds or specialty chemicals that can be recovered and used to offset the cost of CO_2 capture.
- Mineralization converts CO_2 into carbonate rocks, which can be used for soil supplements, construction fill, and other applications.

The Program is collaborating with the National Academies of Science (NAS) to expand the number of projects from industry and academia. The Program is also funding facilities and experiments at the Carbon Sequestration Science Focus Area (CSSFA), which uses in-house resources at NETL to conduct research in a number of sequestration areas with a focus on high technical risk concepts (NETL, 2004b). Examples of R&D efforts are summarized in the following paragraphs.

B.15.1 CO_2 Mineralization

Mineral carbonation, alternately referred to as mineral sequestration, is the reaction of CO_2 with non-carbonate minerals, such as olivine and serpentine, to form geologically stable mineral carbonates. Mineral carbonation can be achieved via two methods. In the first case, minerals can be mixed and reacted with CO_2 in a process plant to produce inert carbonates. In the second, CO_2 can be injected into selected underground mineral deposits, similar to geological sequestration, but resulting in carbonation (NETL, 2000).

- Using mineral carbonation to reduce CO_2 emissions has potential advantages, including:
- Long-term stability of carbonates

- Natural abundance of suitable compounds for binding CO_2
- Economic feasibility of the conversion process

However, mineral carbonation processes will be practical only when two key issues are resolved. First, a fast reaction route must be found that optimizes energy management. Second, issues need to be quantified and addressed pertaining to the mining and processing activities required for mineral sequestration, especially concerns related to overall economics and environmental impacts.

The Mineral Carbonation Program is being managed through NETL's Environmental Product Division and is supported by the Coal Utilization Science, University Coal Research, and the Advanced Metallurgical Processes programs (NETL, 2000). The primary goal of the study is to generate a useful knowledge base that can lead to development of mineral CO_2 sequestration methods. To achieve this goal, the reaction mechanisms, heat requirements, and environmental interactions must be understood well enough to permit the development of engineering processes. A secondary goal is to acquire knowledge essential to understanding the reactions of CO_2 with underground minerals in support of DOE's geological sequestration programs, where CO_2 may be injected into deep saline formations or depleted oil or gas reservoirs. Knowledge of the reaction characteristics of CO_2 with various minerals at elevated pressures and temperatures, such as those found deep underground, will help scientists predict the long-term effects of such practices.

Progress to date has been extremely encouraging. Research has found that finely ground serpentine ($Mg_3Si_2O_5(OH)_4$) or olivine (Mg_2SiO_4) will react with CO_2 in solutions of supercritical CO_2 and water to form magnesium carbonate ($MgCO_3$). When the effort first started, it required 24 hours to produce a 50 percent carbonation level using an olivine feedstock at reaction temperatures of 150-250°C and pressures of 85-100 bar. Through careful control of solution chemistry, the process has been accelerated so that 84 percent conversion of olivine can be achieved in just 6 hours. Furthermore, when heat pretreated serpentine is reacted using the same enhanced reaction process, approximately 80 percent conversion occurs in less than an hour. Carbonation studies are continuing with highly instrumented reactors and atomic-level simulations to optimize reaction conditions and explore the use of catalysts and alternative feedstocks.

B.15.2 Process Design for the Biocatalysis of Value-Added Chemicals from Carbon Dioxide

Researchers from the University of Georgia Research Foundation will conduct a novel project awarded by NETL in early 2004 (NETL, 2004l). They will perform metabolic engineering to create strains of microbes that absorb CO_2 and produce byproducts such as succinic, malic, and fumeric acids, all of which have commercial value. The advantage of the proposed process is that microbial strains will be placed in direct contact with the gases emitted from power plants, thereby avoiding the cost of commercial CO_2 capture systems.

B.15.3 Capture and Sequestration of CO_2 from Stationary Combustion Systems by Photosynthesis of Microalgae

A team led by Physical Sciences, Inc. is performing a project to characterize types of flue gas and determine which separation and cleanup technologies are necessary to maximize the conversion of CO_2 by microalgae photosynthesis (NETL, 2004o). Certain species of microalgae that can withstand the harsh conditions associated with flue gas have optimal rates of carbon fixation and have the ability to convert CO_2 into inorganic carbonates. The primary project goal is to develop technologies pertaining to: (1) the treatment of effluent gases from fossil fuel combustion systems; (2) the transfer of CO_2 into aquatic media; and (3) the efficient conversion of CO_2 by photosynthetic reactions to materials for reuse or sequestration. The objectives of this project are to design an industrial-scale sequestration system for combustion units and model the sequestration process to perform an economic analysis and provide cost-effective solutions.

By early 2004, the project had tested 50 strains of microalgae for growth at different temperatures; analyzed 34 strains for high-value pigments; tested 21 strains for tolerances to simulated flue gases; and tested 28 strains for potential carbon sequestration into carbonates for long-term storage. The researchers also tested a CO_2 removal process, a CO_2 injection device, process control devices, and an algae separation process for a scaled-up photo-bioreactor.

B.15.4 Enhanced Practical Photosynthetic CO_2 Mitigation

Ohio University, Montana State University, and Oak Ridge National Laboratory are performing a NETL-sponsored project to demonstrate the technical and economic feasibility of an enhanced photosynthetic system that takes up CO_2 from flue gases at power plants (NETL, 2004p). The desired systems will separate sunlight into spectral regions to maximize the growth of photosynthetic cyanobacteria. The goal is to have a self-powering system that can reduce CO_2 emissions onsite in a relatively compact space.

Besides mitigating CO_2 emissions, this novel method of photosynthetic sequestration could provide three other benefits. First, it would generate oxygen, which is a natural product of photosynthesis. Second, it would reduce gaseous pollutants, because the flow process used to enhance the soluble carbon concentration is a natural scrubber. The NO_X would be converted to nitrates, SO_x would be converted to sulfates and sulfites, and any NH_3 that might slip through an upstream Selective Catalytic Reduction (SCR) process for NO_X reduction would be scrubbed as well. Such scrubbing is beneficial to photosynthesis, because the microalgae require nitrogen to grow. Third, it would produce biomass for beneficial end-uses; microalgae have been used as soil stabilizers and fertilizers, in the generation of biofuels (biodiesel and ethanol), and in the production of hydrogen for fuel cells. Microalgal biomass has also shown suitable ignition characteristics for co-firing in pulverized coal-fired generation units.

Other NETL-sponsored studies are also investigating natural processes in algae and bacteria for use in innovative carbon sequestration (NETL, 2005b):

- The INEEL is studying the use of cyanobacteria as a biofilm with the aim of optimizing its physiology for efficient photosynthesis and CO_2 saturation.
- The University of North Dakota Energy and Environmental Research Center is evaluating the use of microalgae for onsite removal of CO_2 from flue gas.
- California State University San Marcos is performing a study of potential carbon sequestration through the conversion of CO_2 to calcium carbonate by coccolithophorid algae.

B.16 NON-CO_2 GREENHOUSE GAS MITIGATION

Non-CO_2 emissions from human-related activities contribute approximately 20 percent of the manmade greenhouse effect. Since many non-CO_2 GHG have significant economic value, their emissions can often be avoided or captured at a low net cost.

Methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), ozone (O_3), and other gases have different measures of effectiveness at absorbing infrared (heat) radiation from the earth and holding it in the atmosphere, which is called the global warming potential (GWP). Table C-

1 shows the major GHG, their historic and current atmospheric concentrations, and their GWP values over a 100-year time horizon relative to CO_2.

Table C-1. Comparison of Greenhouse Gases

Gas	Pre-1750 Tropospheric Concentration	Current Tropospheric Concentration	GWP 100-yr	Lifetime in Atmosphere (years)
Carbon Dioxide	280 ppm	370 ppm	1	Variable
Methane	709 ppb	1,786 ppb	23	12
Nitrous Oxide	270 ppb	315 ppb	296	114
CFCs (-11, -12, -113)	0	885 ppt	4,600 – 10,600	45 – 100
Others	0	311ppt	140 – 22,200	<5 – 10,000

ppm – part per million , ppb – parts per billion , ppt – parts per trillion

GWP – global warming potential, relative to CO_2 GWP of 1.0.

(Source: NETL, 2005b)

The Carbon Sequestration Program focuses on areas in which non-CO_2 GHG abatement is integrated with energy production, conversion, and use. The Program also works with the EPA Methane and Sequestration Program to assess the role of non-CO_2 GHG emissions abatement actions in a nationwide strategy for reducing GHG emissions intensity, and to identify priority areas for research and development (NETL, 2005b). Examples of R&D efforts are summarized in the following paragraphs.

- The Yolo County (California) Department of Planning and Public Works is constructing a full-scale bioreactor landfill as a part of the EPA's Project XL program to develop innovative waste management approaches while providing superior GHG emissions protection (NETL, 2003l). NETL is a co-sponsor for the project.
- In a bioreactor landfill, controlled quantities of liquid (leachate, groundwater, grey-water, etc.) are added and recirculated as necessary to maintain the waste at or near its moisture holding capacity. This process significantly increases the biodegradation rate of the waste and thus decreases the waste stabilization and decomposing time (5 to 10 years) relative to what would occur within a conventional landfill (30 to 50 years or more). If the waste decomposes anaerobically (in the absence of oxygen), it produces landfill gas that is primarily methane, a GHG. Methane is over 20 times more potent than CO_2 in its effects on the atmosphere. This byproduct of anaerobic landfill waste decomposition can be a substantial renewable energy resource that can be recovered for power generation or other uses.
- In the initial phase of this project, a 12-acre landfill module was constructed consisting of several cells. The cells include instrumentation to monitor bioreactor performance. The final phase, pertaining to carbon sequestration, involves evaluating full-scale performance and potential of aerobic and anaerobic bioreactor landfill cells as tools for abating GHG emissions resulting from organic waste decomposition in landfills.

B.16.1 Mine-mouth Ventilation Methane Mitigation

Consol Energy, Inc. and MEGTEC Systems are performing a project co-funded by EPA and NETL to design, build, and operate for 12 months a commercial-scale thermal flow reversal reactor (TFRR) interfaced with a working coal mine ventilation fan to reduce emissions of methane (NETL, 2004q). The TFRR technology employs the principle of regenerative heat exchange between a gas and a solid bed of a heat exchange medium. Ventilation air methane flows into and through the reactor in one direction, and the temperature is increased until the methane is oxidized. The hot products of oxidation then lose heat as they continue toward the far side of the bed. At a specified interval, the flow is automatically reversed, so that the hot part of the bed heats the incoming gas. Through the use of heat exchange, excess heat may be transferred for local heating needs or for the production of electric power. The TFRR will oxidize 95 percent of the methane in the vent stream to CO_2, thereby reducing its global warming potential by 87 percent.

B.16.2 Coal Mine Waste Methane Utilization

DOE prepared a draft Environmental Assessment to evaluate potential impacts from the construction and operation of an Integrated Power Generation System for Coal Mine Waste Methane Utilization (NETL, 2002p). DOE's objective for participating in a cooperative agreement with Northwest Fuel Development, Inc. was to support the demonstration of a technology having the potential to reduce methane emissions from coal mines. Specifically, DOE intended to provide partial funding (approximately 35 percent of the total project cost) to demonstrate the application of a system which would collect "gob gas" (waste methane from the mined out portion of an underground mine following extraction of the coal using long-wall mining), upgrade the gas by removing impurities (primarily water, carbon dioxide, and nitrogen), and use the fuel gas in a series of 18 modular reciprocating internal combustion engines driving electrical generators to produce electricity for use at the mine. A portion of the gas meeting pipeline quality standards would be sold to the local gas distribution company.

B.16.3 Upgrading Methane Streams with Ultra-fast Thermal Swing Adsorption (TSA)

The separation of nitrogen from methane is one of the most significant challenges in recovering low-purity methane streams. In a project sponsored by NETL, Velocys, Inc. will focus on the separation of nitrogen from methane by applying a proprietary modular microchannel process technology (MPT) to achieve ultra-fast thermal swing adsorption (TSA). The primary goal of this project is to design and demonstrate a revolutionary approach for upgrading low-BTU methane streams from coalmines, landfills, and other sources (NETL, 2004r). MPT employs small process channels to greatly enhance heat and mass transfer. Enhanced heat transfer yields TSA cycle times of seconds compared to hours for conventional TSA systems and enables compact, economic systems for upgrading methane streams to pipeline quality.

The project is being conducted in two phases. The objective of the first phase is to assess the technical and market feasibility of an MPT-based TSA approach for upgrading low-BTU methane streams. The objective of the second phase is to conduct bench-scale demonstration of Ultra-fast TSA. Thus far, preliminary tests have been initiated and include the collection of methane and nitrogen capacity over several temperatures, compositions, and pressures.

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